

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-208939

(43)Date of publication of application : 13.08.1996

(51)Int.Cl.

C08L 51/04
C08L 51/04
C08K 3/22
C08K 5/02
//(C08L 51/04
C08L 83:04)

(21)Application number : 07-016944

(71)Applicant : ASAHI CHEM IND CO LTD

(22)Date of filing : 03.02.1995

(72)Inventor : YAMAMIYA REI
FUJITA TOMOYUKI

(54) SELF-EXTINGUISHING FLAME-RETARDANT POLYSTYRENE RESIN COMPOSITION HAVING DRIPPING PROPERTY

(57)Abstract:

PURPOSE: To obtain a styrene resin composition having such excellent self-extinguishing properties that it can be used in the fields of housings and components of business machines, information equipments, etc., which need to have especially self-extinguishing properties and being also excellent in a balance among heat resistance, impact resistance and heat stability.

CONSTITUTION: This self-extinguishing flame-retardant polystyrene resin composition comprises 100 pts.wt. rubber-modified polystyrene resin (A), 4-8 pts.wt. tetrabromobisphenol A and polyhalogenated aliphatic ether (B), a polyhalogenated diphenyl-alkane (C) in an amount being equivalent to 20-50 % of the number of pts.wt. of B and giving 10 pts.wt. or below total of B and C, antimony trioxide (D) in an amount equivalent to 20-50% of the number of pts.wt. of A and 0.0005-0.05wt.% (in terms of the weight of the silicon atoms), based on the total of A to D, orgabopolysiloxane (E).

LEGAL STATUS

[Date of request for examination] 24.01.2002

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
 2. *** shows the word which can not be translated.
 3. In the drawings, any words are not translated.
-

CLAIMS**[Claim(s)]**

[Claim 1] (A) It is number of copies which is [derivative / ether / of (B) tetrabromobisphenol A and the poly halogenated aliphatics] equivalent to 20 - 50% of addition number of copies (above-mentioned / B /) to the rubber denaturation polystyrene system resin 100 weight section in 4 - 8 weight section and (C) poly halogenation diphenyl alkane. And it is added so that the sum of addition number of copies of (B) and (C) may become below 10 weight sections. Furthermore, the (D) antimony trioxide is consisted of number of copies equivalent to 20 - 50% of addition number of copies (above-mentioned [B]). The above (A) Self-reduction-of-inflammation nature polystyrene system fire retardancy resin constituent which has the dropping nature characterized by adding (E) organic polysiloxane to the total quantity of - (D) so that it may become the 0.0005 - 0.05 % of the weight of the amount of silicon.

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the polystyrene system resin constituent excellent in the balance of thermal resistance, shock resistance, and thermal stability while it is excellent in self-reduction-of-inflammation nature by having dropping nature in detail about a styrene-resin constituent. Especially as Field of the Invention, the still more detailed use effective in back covering of TV, VTR device housing and a chassis, printer housing, FAX housing, a toner cartridge, a toner bottle, a panelboard, etc. of housing of a business-machine machine and information machines and equipment, parts, etc. is expected to the field and concrete target of which self-reduction-of-inflammation nature is required.

[0002]

[Description of the Prior Art] The styrene resin is used over the reason of the outstanding fabricating-operation nature, a mechanical characteristic, and an electrical property in many fields. However, since it is a flammability, flameproofing of a resin is needed in case it is used for parts housing of OA equipment and home electronics and the electrical and electric equipment, and electronic-related etc. It is regulated by UL etc. about this fire retardancy, and the means of flameproofing various in recent years is examined. In the housing field of home electronics, the above-mentioned flameproofing regulation and thermal resistance, shock resistance, and thermal stability are called for into it, and the styrene resin which maintained the balance which fills all these military requirements is called for. Generally, as flameproofing of a rubber denaturation vinyl aromatic resin, independent or adding by combined use are shown in JP,62-4737,A, JP,54-44298,B, JP,54-68854,B, etc. in halogen system flame retarders, such as a polymer of a halogen content epoxy polymer, tetrabromobisphenol A (TBA), and a TBA and an alkyl halide.

[0003] However, when it blends with thermoplastics, above TBA has the fault of reducing thermal resistance greatly, and its thermal stability is not desirable, either. . Moreover, in order to prevent a heat-resistant fall, using together and using high-melting point type halogen system flame retarders, such as deca BUROMO diphenyloxide (DBDPO), and an antimony trioxide is shown in JP,58-187450,A. However, there was a problem of degradation of the badness of the dispersibility of a flame retarder and the lightfastness of mold goods as a fault of such a flame retarder. Furthermore, using together and using a bromination bisphenol A type epoxy resin and an antimony trioxide as a flame retarder solving the above problem is shown in JP,63-72749,A. However, when the flame retarder of the amount which gives the self-reduction-of-inflammation nature which may be satisfied as a fault of this flame retarder was added, there was a problem that shock resistance fell.

[0004] Moreover, a lot of flame retarders are required for the above-mentioned flameproofing technology as fire-resistant level for the purpose of V-0 rank of UL94 of the U.S. undershirt rye TAZU laboratory in corporation (Underwriters Laboratories Inc., U.S.A), and the fall of physical properties is not escaped. On the other hand, although there is a combustion rank called V-2 in UL94 and it is inferior to above V-0 as an inflammable rank, curtailment of the addition of a flame retarder is possible. although the hexa BUROMO cyclo dodecane (HBCD) is shown in JP,38-16837,B and JP,62-34784,B as technology aiming at V-2 of UL94 as an outstanding added type flame retarder of thermal resistance, lightfastness, and shock resistance and it is generally used, this flame retarder has the low decomposition temperature of a flame retarder, and when it kneads to thermoplastics, it has the fault which will be said if the thermal stability of a resin falls remarkably

[0005] Moreover, although attaining V-2 with the ether derivative of tetrabromobisphenol A and the poly halogenated aliphatics is shown in JP,5-140389,A, it is made indispensable for the above-mentioned compound to have a toxic problem, and to use a stabilizer together. Moreover, although it is shown that V-2 attains with the compound obtained by the multiple address by the reaction of the end of TBA and the alkyl halide of carbon numbers 1-5, if only this

compound is used as a flame retarder, since the bromine content is low, a lot of addition will be required and will bring about the fall of thermal resistance and thermal stability.

[0006] Even when what halogen system flame retarder is furthermore chosen as JP,6-43542,B Although the purport publication of the fire-resistant resin constituent which has dropping nature easily is obtained and carried out if the rubber denaturation styrene resin whose average rubber particle size obtained by carrying out the graft polymerization of the aromatic vinyl monomer to a conjugated-diene system gum polymer is 1-3 micrometers is used In order to raise a fire-resistant performance, the fire-resistant resin constituent described in this official report contains an organic polysiloxane, there is and the purport publication is carried out. [no] For the reason, it is inferior by the physical-properties side, especially the impact strength.

[0007]

[Means for Solving the Problem] Then, this invention persons solved the technical problem of the above-mentioned conventional technology, and research was repeated wholeheartedly that the polystyrene system fire retardancy resin excellent in the balance of the fire retardancy by having good dropping nature and thermal resistance, shock resistance, and thermal stability should be developed. Consequently, by blending with a polystyrene system resin combining two sorts of specific halogen system flame retarders, and a fire-resistant assistant, it finds out attaining the polystyrene system fire retardancy resin excellent in the balance of the self-reduction-of-inflammation nature according to decreasing the total addition of a halogen system flame retarder, and having good dropping nature rather than adding each flame retarder independently and thermal resistance, shock resistance, and thermal stability, and comes to complete this invention.

[0008] Namely, this invention receives the (A) rubber denaturation polystyrene system resin 100 weight section. (B) It is number of copies which is [derivative / ether / of tetrabromobisphenol A and the poly halogenated aliphatics] equivalent to 20 - 50% of addition number of copies (above-mentioned / A /) in 4 - 8 weight section and (C) poly halogenation diphenyl alkane. And it is added so that the sum of addition number of copies of (B) and (C) may become below 10 weight sections. Furthermore, the (D) antimony trioxide is consisted of number of copies equivalent to 20 - 50% of addition number of copies (above-mentioned [A]). The above (A) The self-reduction-of-inflammation nature polystyrene system fire retardancy resin constituent which has the dropping nature characterized by adding (E) organic polysiloxane to the total quantity of - (D) so that it may become the 0.0005 - 0.05 % of the weight of the amount of silicon is offered.

[0009] this invention is explained in detail below. The rubber denaturation polystyrene system resin (A) used by this invention says the polymer which a rubber-like polymer comes to distribute in the shape of a particle into the matrix which consists of a vinyl aroma polymer, generally a rubber-like polymer is dissolved in a vinyl aromatic monomer (and liquid which added the inert solvent), and churning, a bulk polymerization, a massive suspension polymerization, or solution polymerization is performed, and although obtained by depositing and particle-izing a rubber-like polymer, it is not limited to a polymerization method. As the above-mentioned vinyl aromatic monomer, although alpha-alkylation styrene, such as nucleus alkylation styrene, such as o-methyl styrene besides styrene, p-methyl styrene, m-methyl styrene, 2, 4-dimethyl styrene, ethyl styrene, and p-tertiarybutyl styrene, an alpha methyl styrene, and an alpha-methyl-p-methyl styrene, etc. can be mentioned, a typical object is styrene. These may use together the two or more sorts.

[0010] Moreover, as the aforementioned rubber-like polymer, although a polybutadiene, a styrene butadiene copolymer, a polyisoprene, a butadiene isoprene copolymer, natural rubber, and an ethylene propylene rubber can be mentioned, generally a polybutadiene and a styrene butadiene copolymer are desirable. It is usually that the weight average molecular weight of the matrix portion of the rubber denaturation polystyrene system resin which constitutes the resin constituent of this invention is adjusted to 15x10⁴ or more ranges from a strong relation, and if less than this, intensity will fall rapidly. Although there are especially no restrictions about the rubber-like polymer content of the above-mentioned rubber denaturation polystyrene system resin, generally it is 6 - 12 % of the weight more preferably four to 15% of the weight. Furthermore, the mean particle diameter of the rubber particle in the above-mentioned rubber denaturation polystyrene system resin is controlled by the range of 0.5-6.0 microns. Moreover, although the gel content (toluene insoluble) of the aforementioned rubber denaturation polystyrene system resin is adjusted to 15 - 40% of the weight of a conventional method, it is 20 - 35 % of the weight more preferably.

[0011] As an example of the halogenated compound (B) used by this invention, the designation of the ether derivative of the poly halogenated aliphatics is carried out to tetrabromobisphenol A. Dibromopropane, a TORIBUROMO pentane, a tetrabromo hexane, etc. are mentioned as an example of the poly halogenated aliphatics. Dibromopropane is suitably used from the ease of manufacture especially. About the manufacture method of the above-mentioned flame

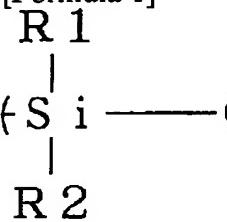
retarder, although various **** are obtained by the method indicated by JP,49-125348,A, JP,49-20155,A, JP,4-270236,A, JP,4-270237,A, etc., it is not limited to a synthesis method.

[0012] In addition, the tradename [a halogenated compound (B)] by Teijin Chemicals incorporated company which can appropriate a commercial object; it is also possible to use FG3100 and tradename;SR720 by Dai-Ichi Kogyo Seiyaku Co., Ltd. Next, although there are a dibromo phenyl, a TORIBUROMO phenyl, a tetrabromo phenyl, pentabromophenyl, dichlorophenyl, a TORIKURORO phenyl, tetrapod chlorophenyl, pentachlorophenyl, etc., a pentabromophenyl machine is desirable as an example of the phenyl group of the halogenation of the poly halogenation diphenyl alkane (C) in this invention, especially from the height of the flameproofing effect also in it.

[0013] Although especially the process of a poly halogenation diphenyl alkane (C) is not limited, you may use what was manufactured by the method indicated by JP,2-42031,A or JP,6-73268,A, for example. It is also possible to appropriate a commercial thing as a poly halogenation diphenyl alkane used for this invention, for example, Saytex8010 of Albemarle, the U.S., is mentioned. The antimony trioxide which is the (D) component of this invention is an object which acts as a fire-resistant assistant. Furthermore, the organic polysiloxane used for this invention can also use [that a structural unit which it is the polymer which contains in a skeleton the repeat of the structural unit generally shown by the following formula, for example, poly dimethylsiloxane, a polyphenyl siloxane, a poly methylphenyl siloxane, etc. are mentioned, and is different not only in the repeat of single structure is random, or] a block or the polymer which is carrying out graft copolymerization.

[0014]

[Formula 1]



[0015] (However, R1 and R2 express an organic machine.)

Moreover, it is also possible to use the polymer which contained other organic machines in the range which does not spoil the character of an organic polysiloxane into the end of this polymer or a chain, and two or more sorts of organic polysiloxanes may be mixed and used. Poly dimethylsiloxane is suitably used especially for this invention. Although especially the repeat number of unit n of an organic polysiloxane is not limited, in the case of a liquefied polysiloxane, the thing of 100,000cSt(s) is used for the viscosity in 25 degrees C from 10, and the thing of 100 to 3,000 is preferably used still more preferably 10,000 cSts from 50. The organic polysiloxane of hypoviscosity has the flash point low disadvantageous for flameproofing, and its possibility of the volatilization at the time of a granulation and the plate out at the time of molding is high. A hyperviscous organic polysiloxane has a problem in the uniform distribution at the time of constituent mixture on the contrary.

[0016] Especially as a method of adding an organic polysiloxane to the polystyrene system fire retardancy resin constituent of this invention, although not limited, it is also possible to add, in case it adds at the time of the polymerization of the above-mentioned (A) rubber denaturation polystyrene system resin or (B), (C), etc. are kneaded with (A) rubber denaturation polystyrene system resin.

(A) These blending ratio of coal to the rubber denaturation polystyrene system resin 100 weight section (B) The ether derivative of tetrabromobisphenol A and the poly halogenated aliphatics 2 - 10 weight section, It is number of copies which is preferably equivalent to 20 - 50% of addition number of copies (above-mentioned [A]) in 4 - 8 weight section and (C) poly halogenation diphenyl alkane. And below 12 weight sections, it is added so that it may become below 10 weight sections preferably, and the sum of addition number of copies of (B) and (C) adds number of copies which is further equivalent to 20 - 50% of addition number of copies (above-mentioned [A]) in the (D) antimony trioxide. It is difficult to maintain good fire retardancy with (B), (C), and (D) being below the ranges of the above-mentioned addition. Conversely, it not only has a bad influence on dynamics properties, such as an impact strength of a resin, as it is beyond the range of the above-mentioned addition, but it checks good dropping resolution nature.

Especially, the time which resolution takes to the loadings of (C) as it is below a convention range to the loadings of (B) becomes long, and dropping nature is checked as it is beyond a convention range. Moreover, the time which resolution takes to the loadings of (D) as it is below a convention range to the loadings of (B) becomes long, and the impact strength of a resin is reduced as it is beyond a convention range. It is required to add (E) organic polysiloxane to

the total quantity of above-mentioned (A) - (D), on the other hand, so that it may become the 0.0005 - 0.05 % of the weight of the amount of silicon, when fewer as an amount of silicon than 0.0005 % of the weight, shock resistance falls, and when [than 0.05 % of the weight] more, a reduction-of-inflammation performance is reduced remarkably.

[0017] The manufacture method of the fire-resistant resin constituent of this invention depends each of these components on carrying out specified quantity combination. Especially the combination method does not have a limit and has the method of a Henschel mixer, a tumbler mixer, a super mixer, a Banbury mixer, a kneader, a roll, a monopodium extruder, a 2 shaft extruder, etc. To this invention constituent, other additives, for example, a fire-resistant assistant, a plasticizer, lubricant, a stabilizer, an ultraviolet ray absorbent, a bulking agent, a coloring agent, a reinforcing agent, etc. can be added in the range which does not spoil the purpose of this invention if needed.

[0018]

[Example] Although an example and the example of comparison are given to below and this invention is explained to it, this invention is not limited at all by these examples. In addition, in the following examples and examples of comparison, many properties of the various rubber denaturation vinyl aromatic resins by which flameproofing was carried out were measured by the following method, and were evaluated.

(1) Izod impactive strength : by ASTM-D256, it measured using the test piece with a notch at 23 degrees C.

(2) Bending elastic modulus : it measured by ASTM-D790.

(3) Heating deformation temperature : it measured by ASTM-648.

(4) Fluidity : the melt flow rate was measured by ASTM-D1238.

(5) Flammability : it examined based on the test method indicated by the "combustion test of the plastic material for parts of a UL94 safety-standard:device" published from the U.S. undershirt rye TAZU laboratory in corporation (Underwriters Laboratories Inc., U.S.A), and the rank of 94V-2 (it abbreviates to "V-2" below) estimated. Moreover, the existence of dropping at the time of a combustion test and the existence of resolution by the dropping were observed.

[0019]

[Examples 1-3 and the examples 1-8 of comparison]

(A) It is an ether derivative of (B) tetrabromobisphenol A and the poly halogenated aliphatics to the 100 weight sections about polybutadiene denaturation polystyrene. FG3100 (front Naka B and publication) by Teijin Chemicals incorporated company It considers as (C) poly halogenation diphenyl alkane. Albemarle Saytex8010 (front Naka C and publication) Specified quantity mixture of TSF 451-100 by Toshiba Silicone, Inc. is further carried out at a rate shown in the table as the (D) antimony trioxide (front Naka D and publication) and a (E) organic polysiloxane. melting kneading (cylinder setting temperature of 220 degrees C) was carried out with the biaxial extruder -- after injection molding (cylinder setting temperature of 200 degrees C) was carried out, and the test piece was created

[0020] Izod impactive strength, a bending elastic modulus, a heating deformation temperature, and flammability were measured using this test piece, respectively. However, inflammable evaluation showed the existence of dropping at the time of the judgment by the above-mentioned specification of UL94, and a combustion test, and the existence of resolution according to the dropping further in the table. Moreover, fixed time stay of the resin which corned by the above-mentioned method was carried out at 260 degrees C of cylinder temperatures with the injection molding machine, and thermal stability ability was evaluated.

[0021]

[Table 1]

	単位	実施例1	実施例2	実施例3	比較例1	比較例2	比較例3	比較例4	比較例5	比較例6	比較例7	比較例8
ゴム変性ポリスチレン樹脂	部	100	100	100	100	100	100	100	100	100	100	100
B	部	4	6	8	4	4	10	4	12	0	8	4
C	部	1	3	2	3	1	4	1	0	10	2	1
D	部	1	3	2	1	0	2	6	0	4	2	1
B+C	部	5	9	10	7	5	14	5	12	10	10	5
E	重量%	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.1	0.0001
74ゲット衝撃強度	kgcm/cm	9	8	8	9	9	5	5	7	5	9	5
曲げ弾性率	kgf/cm ²	25,000	25,000	25,000	25,000	25,000	27,000	27,000	26,000	27,000	25,000	27,000
加热変形温度	℃	80	79	78	80	80	76	80	75	82	78	80
燃焼性		V-2	V-2	V-2	OUT	OUT	V-2	OUT	V-2	OUT	OUT	V-2
滴下		あり	あり	あり	あり	あり	あり	なし	あり	なし	あり	あり
滴下消炎		あり	あり	あり	なし	なし	あり	なし	あり	なし	なし	あり
熱安定性		○	○	○	○	○	○	○	○	○	○	○

* Eは添加された有機ポリシロキサンの樹脂全体に対する珪素含有量（重量%）を示す。

* 下線は請求範囲外の添加量または使用不可能な物性値であることを示す。

[0022]

[The examples 9-11 of comparison] After carrying out specified quantity mixture at a rate which showed the deca BUROMO biphenyl ether (Dai-Ichi Kogyo Seiyaku; PIROGADO SR- 250), tetrabromobisphenol A (; by Teijin Chemicals incorporated company FG2000), and the hexa BUROMO cyclo dodecane (; by Dai-Ichi Kogyo Seiyaku Co., Ltd. PIROGADO SR- 103) in the table to the 100 weight sections, respectively and carrying out melting kneading (cylinder setting temperature of 220 degrees C) of the polybutadiene denaturation polystyrene with a biaxial extruder, injection molding was carried out and the test piece was created. Izod impactive strength, a bending elastic modulus, a heating deformation temperature, and flammability were measured using this test piece, respectively. However, inflammable evaluation showed the existence of dropping at the time of the judgment by the above-mentioned specification of UL94, and a combustion test, and the existence of resolution according to the dropping further in the table. Moreover, fixed time stay of the resin which corned by the above-mentioned method was carried out at 260 degrees C of cylinder temperatures with the injection molding machine, and thermal stability ability was evaluated.

[0023]

[Table 2]

	単位	比較例9	比較例10	比較例11
ゴム変性ポリスチレン樹脂	部	100	100	100
B	部	0	0	0
C	部	0	0	0
B+C	部	0	0	0
ハイブリッドクロロドテック	部	3	0	0
テトラフロモビスフェノールA	部	0	10	0
テカフロモビスフェノオキサト	部	0	0	12
D	部	1	3	3
E	重量%	0.005	0.005	0.005
フレイムチャーチ強度	kg/cm ²	9	6	5
曲げ弾性率	kgf/cm ²	25,000	26,000	27,000
加熱変形温度	°C	80	75	82
燃焼性		V-2	OUT	V-2
滴下		あり	あり	あり
滴下消炎		あり	なし	あり
熱安定性		×	○	○

[0024]

[Effect of the Invention] In order to blend the resin constituent of this invention with a styrene resin at a specific rate like a ** top combining two sorts of specific flame retarders, while excelling in self-resolution nature by having dropping nature, it excels in the balance of thermal resistance, shock resistance, and thermal stability. Therefore, the still more detailed use effective in back covering of TV, VTR device housing and a chassis, printer housing, FAX housing, a toner cartridge, a toner bottle, a panelboard, etc. of housing of a business-machine machine and information machines and equipment, parts, etc. is expected to the field and concrete target by which self-resolution nature is demanded especially of the resin constituent of this invention.

[Translation done.]